# Van der Waals molecules

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The information currently available on the properties and interactions of van der Waals molecules is reviewed. Methods for producing and detecting these molecules are discussed. The properties of van der Waals molecules found from measurements of the rotational spectra of molecules by the method of molecular-beam electric resonance spectroscopy are reported. The photoionization and photodissociation of van der Waals molecules are analyzed.

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## 1. INTRODUCTION

A van der Waals molecule is one consisting of gas atoms or molecule, e.g., $(Ar)_2$, $(N_2)_2$, and $Na{\cdot}H_2$. The binding in these molecules is provided by the long-range van der Waals interaction. The exchange interaction in these molecules, which corresponds to the overlap of the electron shells of the interacting particles, is a repulsion. The bond rupture energy in a van der Waals molecule is thus relatively low, of the order of $10^{-2}$ eV. It follows that under ordinary conditions the relative number of van der Waals molecules in a gas is extremely small, and these molecules have no effect on the properties of the gas.

van der Waals molecules are produced effectively at low temperatures, e.g., when a gas flows out of a nozzle (in this case, van der Waals molecules are frequencly called "clusters"). The various interactions of van der Waals molecules are equally important. When a process involves a three-body collision, the presence of van der Waals molecules can substantially accelerate it. The production of negative ions in air, $e + 2O_2 \rightarrow O_2^- + O_2$, for example, may involve van der Waals molecules: $e + (O_2)_2 \rightarrow O_2^- + O_2$. Van der Waals molecules also play an important role in the growth of the formation which nucleate the appearance of a new phase in a gas. The first step in these processes is the formation of van der Waals molecules.

van der Waals molecules have been under study, and the results have been accumulating, for a long time now. In the past decade, however, the development of new experimental apparatus has raised some new possibilities and has opened up some new fields of research. Our purpose in the present review is to present the information available on van der Waals molecules and to describe the present state of the research effort.

## 2. PROPERTIES OF VAN DER WAALS MOLECULES

Among the properties which characterize van der Waals molecules we include geometric properties, which characterize the geometric structure of the molecule and the distance between its components, and energy properties, primarily the energy required to rupture the weak bonds. For the simplest molecules, consisting of gas atoms and molecules, these properties were originally determined by analyzing data on the kinetic coefficients in gases (the diffusion coefficients of atoms and molecules in gases, the thermal conductivity, the viscosity, and the coefficient of the thermal diffusion), on the virial coefficients, and other properties of gases. Information was also extracted from the properties of crystals made up of gas atoms or molecules whch exist at low temperatures. Clearly, if the characteristics of the gas or condensed medium of interest are determined by a binary interaction of the atoms or molecules in the medium, and if the region of attraction of the interacting particles is important, then by choosing an appropriate set of these characteristics one can determine the interaction potential of the atoms or molecules in the attraction region within a corresponding accuracy.

This approach has a rich history (see Ref. 1, for example). At one time, it was the only method available for determining the properties of van der Waals molecules. Thirty years ago, the depth of the well in the interaction potential and the corresponding distance between particles were already known reliably for inert gas molecules consisting of two identical atoms and also for several van der Waals molecules consisting of two diatomic molecules. This information was obtained by the set of methods which we just listed.

Now these methods for finding the properties of van der Waals molecules are progressively giving way to a related

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method which makes of the scattering characteristics of particles. The interaction characteristics of atoms or molecules have recently been extracted from measurements of the total or differential scattering cross section of the particles found at various collision energies. In these methods, as in the earlier methods, the characteristics of the attractive potential of the particles are determined from measurements of properties which are determined by the interaction of the particles. The scattering characteristics of the particles, however, contain fewer averages over the interaction parameters than do the kinetic coefficients, for example, so that the methods based on particle scattering are more informative. Furthermore, these methods can be used just as easily to study the interactions of either identical or different particles, while achieving this versatility was extremely problematical in the earlier approaches. The price we pay for the advantages of the particle-scattering method is that we have to resort to the more-complicated beam technology and also to more-complicated methods for detecting the scattering particles. At the present level of experimental sophistication, however, this presents no problem.

Considerable progress toward an understanding of the structure of van der Waals molecules has been made by the method of molecular-beam electric resonance spectroscopy. This method can reveal the absorption spectrum of van der Waals molecules with a high resolution in the microwave and rf ranges. The configuration of the molecule, its geometric properties, and some of its energy properties can be extracted from the spectra recorded for molecules of various isotopic composition and in external electric fields. This method is applied to molecules which exhibit an effective absorption in the microwave and rf spectral ranges. In practice, therefore, it is used for molecules which consist of a dipole molecule and an inert gas atom or gas molecule. This method is described in more detail in Section 5, where the results which it has yielded are also discussed.

Theory can make a definite contribution to our understanding of the strucutre and energy properties of van der Waals molecules. It is important to note that the conventional methods of quantum chemistry cannot be used in calculations for weak bonds. There are definite possibilities in asymptotic methods for atomic-structure calculations; these methods can determine the properties of the weak bonds quite simply, although with limited accuracy (see Refs. 2 and 3, for example).

We will report results on the interaction properties of the simplest van der Waals molecules. Most of these results have come from experiments on particle scattering. Two types of research are carried out on the elastic scattering of atoms and molecules. In one approach, the total scattering cross section of the particles is determined from the loss of particles from the beam. In the other approach, the differential scattering cross section of the particles is measured. Although it might seem that the differential scattering cross section would yield more information about the interactions of the particles, the customary approach is to measure the relative value of the differential scatering cross section and the absolute value fo the total scattering cross section. For this reason, the two methods are comparable in terms of information content.

Avoiding the details of the experimental methods for studying the scattering of atomic and molecular particles (see Refs. 4–6, for example), we will analyze the possibilities of these methods, and we will report some results. The total scattering cross section is determined by the scattering of the particles through small angles, so that the total cross section provides information about the interaction in the region in which the interaction potential is significantly smaller than the collision energy. The differential cross section usually corresponds to scattering through a large angle. In this case, the scattering is determined by the interaction of the particles in the region in which the interaction potential is comparable to the kinetic energy of the particles. For this reason, measurements of the total and differential scattering cross sections at a given collision energy correspond to different

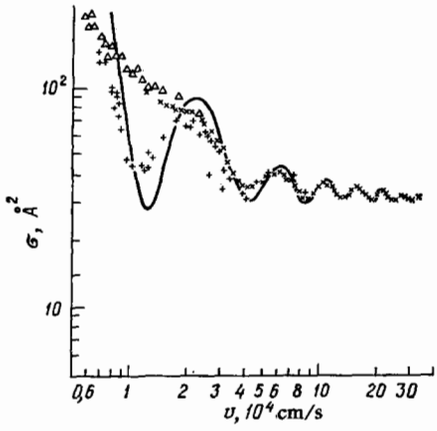


FIG. 1. Total cross section for $^4$He–$^4$He scattering as a function of the relative velocity. Points—experimental[6–8]; curve—theoretical.[9,10]

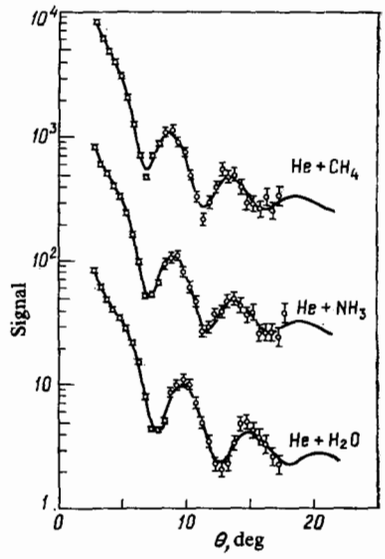


FIG. 2. Relative differential cross section for the scattering of helium atoms by gas molecules as a function of the scattering angle for a relative collision energy of 63 meV (Ref. 11). Points—experimental; curves—calculated for the most suitable particle interaction potential.

TABLE I. Parameters of the potential for the interaction of atoms with inert gas atoms.[12]

| atom | He | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| He | 0,92<br>2,97 | 1,6<br>3,2 | 1,8<br>3,5 | 2,5<br>3,8 | 2,5<br>4,1 |
| Ne | — | 3,7<br>3,1 | 6,0<br>3,5 | 6,0<br>3,7 | 6,1<br>3,8 |
| Ar | — | — | 12,2<br>3,76 | 15<br>3,9 | 15<br>4,1 |
| Kr | — | — | — | 17,2<br>4,0 | 19<br>4,3 |
| Xe | — | — | — | — | 23<br>4,4 |
| H | 0,5<br>3,7 | 2,0<br>3,2 | 4,3<br>3,6 | 6,0<br>3,6 | 6,8<br>3,8 |
| Li | — | 1,0<br>5,1 | 5,3<br>5,0 | 8,5<br>4,9 | 13<br>4,9 |
| Na | — | 1,0<br>5,3 | 4,8<br>5,0 | 8,6<br>4,8 | 13<br>4,8 |
| K | — | 5,6<br>5,0 | 5,6<br>5,0 | 9,0<br>5,0 | 13<br>5,2 |
| Rb | — | 5,4<br>5,0 | 5,6<br>5,2 | 9,1<br>5,3 | 13<br>5,3 |
| Cs | — | 5,0<br>5,0 | 5,8<br>5,2 | 9,2<br>5,4 | 13<br>5,4 |

TABLE II. Spherically symmetric part of the potential for the interaction of atoms and diatomic molecules with gas molecules.[12]

| atom | $H_2$ | $N_2$ | $O_2$ | NO |
|---|---|---|---|---|
| He | 1,3<br>3,5 | 2,4<br>3,7 | 2,8<br>3,5 | 2,3<br>3,7 |
| Ne | 3,1<br>3,3 | 5,5<br>3,6 | 5,8<br>3,4 | 6,2<br>3,1 |
| Ar | 6,5<br>3,4 | 10<br>3,8 | 12<br>3,7 | 12<br>3,6 |
| Kr | 7,8<br>3,7 | 13<br>3,9 | 14<br>3,9 | 14<br>3,7 |
| Xe | 8,4<br>3,9 | 15<br>3,9 | 16<br>3,9 | 17<br>3,8 |
| $H_2$ | 3,0<br>3,4 | 5,6<br>3,5 | 5,6<br>3,7 | 5,9<br>3,6 |
| $N_2$ | — | 3,3<br>3,7 | 3,5<br>3,6 | 3,4<br>3,6 |
| $O_2$ | — | — | 3,8<br>3,5 | 3,9<br>3,5 |

TABLE III. Parameters of the potential for the interaction of inert gas atoms with halogen atoms.

| Halogen atom | State of van der Waals molecule | Ne | Ar | Kr | Xe |
|---|---|---|---|---|---|
| F [13,15–17,19] | $X_{1/2}$ | 5,2<br>2,85 | 12<br>2,95 | 13<br>3,0 | 150<br>2,29 |
| | $A_{3/2}$ | 3,9<br>3,05 | 6,5<br>3,45 | 6,7<br>3,6 | 7,0<br>3,80 |
| Cl [14,18,20] | $X_{1/2}$ | — | — | — | 35<br>3,2 |
| | $A_{3/2}$ | — | — | — | 16<br>4,1 |
| Br [21,22] | $X_{1/2}$ | — | 16<br>3,73 | 20<br>3,90 | 28<br>3,80 |
| | $A_{3/2}$ | — | 11<br>3,93 | 15<br>4,05 | 18<br>4,11 |
| I [21,23] | $X_{1/2}$ | — | — | 24<br>4,05 | 30<br>4,30 |
| | $A_{3/2}$ | — | — | 16<br>4,32 | 21<br>4,60 |

regions of the interaction; i.e., the two types of measurements complement each other.

Figures 1 and 2 show some typical experimenal results on the total and differential scattering cross sections. The particle interaction potental can be extracted from results of this type. The customary approach is to write the interaction potential as an analytic expression with adjustable parameters, use this potential to calculate the scattering cross section, and then choose the parameters in the potential to fit the experimental cross sections.

At relatively modest collision energies, measurements taken with a good resolution reveal oscillations in the particle scattering cross sections (Figs. 1 and 2). The amplitude and the positions of the extrema of these oscillations provide further information about the particle interaction potential. Consequently, measurements of the cross sections for the elastic scattering of particles can provide a detailed picture of the interaction potential. This detailed picture cannot be drawn from the results furnished by the earlier methods, which use integral characteristics of the scattering cross sections such as transport coefficients.

Tables I–III show the characteristic parameters of the interaction potentials of several atomic particles: the depth of the attractive potential, $D_e$, and the distance ($r_m$) between particles which corresponds to the potential minimum.[1)] The depth $D_e$ differs from the dissociation energy ($D_0$) of a van der Waals molecule by the energy of the zero-point vibrations for the given bond.

In connection with the data in Table III we would like to mention yet another special method for reconstructing the interaction potential from information on the spectrum of a molecule. The high resolution with which the spectra of molecules can now be measured makes it possible to determine the positions of those vibrational levels of a molecule between which a radiative transition occurs; from the position of these levels one can ultimately determine the interaction parameters of the molecule for the upper and lower electron states of the transition. Table III is based in part on information extracted from the emission spectra of excimer molecules, which consist of an inert gas atom and a halogen atom. The lower state of the transition in these cases corresponds to the electronic ground state of the interacting atoms.

[1)] In Tables I–III the upper number is the well depth $D_e$ in the interaction potential (in millielectron volts), while the lower number is the corresponding distance ($r_m$) between nuclei, in angstroms.

## 3. METHODS FOR DETECTING VAN DER WAALS MOLECULES

Various methods have been developed for identifying and studying van der Waals molecules. There are the mass-spectrometric methods, IR spectroscopy, microwave and rf spectroscopy, and photoionization in the UV region. We will be discussing most of these methods below, along with the corresponding studies and results. Despite the large variety of methods available for detecting van der Waals molecules, we lack a reliable universal method for measuring their density, because the difficulties in working with van der Waals molecules and the circumstance that these methods have only a brief history. There is the hope that the capabilities of these methods will make it possible to measure reliably the density of van der Waals molecules in the not-too-distant future. In this section of the review we analyze the method of IR spectroscopy and the mass-spectrometric method—the methods most suitable for this purpose.

The infrared absorption spectrum of van der Waals molecules corresponding to vibrational of the molecules which are constituents of the van der Waals molecules differ slightly from the infrared absorption spectrum of the free molecules. The situation is illustrated in Table IV with the positions of the transitions in the $CO_2$ and $N_2O$ molecules in the free state or bound with the same molecules by weak van der Waals bonds. We see that the absorption spectrum of these molecules differs to the extent that it is possible to distinguish spectroscopically $CO_2$ and $N_2O$ molecules from their clusters.

This circumstance makes it possible to single out a part of the spectrum in which van der Waals molecules absorb effectively, while their constituents in the free state do not absorb. By measuring the absorption coefficient of a gas in this part of the spectrum one can determine the relative density of van der Waals molecules.

This method was used in Refs. 26 and 27 to determine the temperature dependence of the equilibrium constants for the reactions $Ar \cdot HCl \rightleftarrows Ar + HCl$ and $Ar \cdot HBr \rightleftarrows Ar + HBr$. Analysis of the results yielded the enthalpy for the breakup of van der Waals molecules: $\Delta H = -1219 \pm 50$ cal/mole ($53 \pm 2$ meV; Ref. 26) for the first reaction and $-1053 \pm 65$ cal/mole ($46 \pm 3$ meV; Ref. 27) for the second.

The line representing a vibrational transition of a molecule may become greatly broadened by the interaction when this molecule becomes part of a van der Waals molecule. The effect is particularly marked in the interaction of two identical molecules, where the vibrational excitation can be easily transferred from one molecule to another. In this case, the broadening of the line corresponding to the vibrational transition may make the absorption coefficient with the van der Waals molecule at the maximum considerably lower than the corresponding value for the free molecule. In this case the density of van der Waals molecules can be determined from the pressure dependence of the density of simple molecules in the pressure region where this dependence is linear. In particular, this approach was taken in Ref. 28 to determine the density of $CO \cdot CO$ van der Waals molecules.

The mass-spectrometric method can determine the relative number of van der Waals molecules in gas, but this determination requires additional information about the processes involved. Let us examine this method. It involves taking a small sample of the gas and partially ionizing it with electrons, so that the ratio of currents for ions of different species can be measured. Let us assume, for example, that a gas consists of atoms or molecules of species $A$ and $B$ and also van der Waals molecules $A \cdot B$. The ionization then involves the reactions

$$\begin{aligned} e + A &\xrightarrow{\sigma_1} A^+ + 2e, \\ e + A \cdot B &\begin{cases} \xrightarrow{\sigma_2(1-f)} AB^+ + 2e, \\ \xrightarrow{\sigma_2 f} A^+ + B + e, \end{cases} \end{aligned} \tag{1}$$

where the symbols above the arrows are the corresponding rate parameters. We see that in order to reconstruct the fraction of van der Waals molecules we need to know the ratio of $\sigma_2$, the cross section for electron-impact ionization of the van der Waals molecules, to $\sigma_1$, the cross section for ionization of the simple molecules; we also need to know the probability ($f$) for the formation of the simple ions upon ionization of the van der Waals molecules. Knowing these properties, we can construct the ratio of the density [A] of simple molecules to the density [A · B] of van der Waals molecules:

$$\frac{[A]}{[A \cdot B]} = \frac{\sigma_2 (1-f)}{\sigma_1} \left( \frac{j_{A^+}}{j_{AB^+}} - \frac{f}{1-f} \right), \tag{2}$$

where $j$ is the current of the ions of the corresponding species.

TABLE IV. Transition frequencies (in reciprocal centimeters) for vibrational transitions of $CO_2$ and $N_2O$ molecules and their combinations.[24-25]

| Molecule | Transition* | $CO_2$ molecule or $N_2O$ molecule | $(CO_2)_2$ or $(N_2O)_2$ dimer | $CO_2$ or $N_2O$ crystal |
|---|---|---|---|---|
| $CO_2$ | $\nu_1 + \nu_3$ | 3716 | 3714.8 | 3711.5 |
| $CO_2$ | $2\nu_2 + \nu_3$ | 3609 | 3605 | 3596.5 |
| $N_2O$ | $\nu_3$ | 2223.5 | 2233 | 2240 |

*Here $\nu_1$ represents the vibrations of the two oxygen atoms in the $CO_2$ molecule along the axis of the molecule in the case in which these two oxygen atoms lie at identical distances from the carbon atom; $\nu_2$ corresponds to deformation vibrations of the oxygen atoms in the direction perpendicular to the axis of the molecule; and $\nu_3$ corresponds to the antisymmetric vibrations of the atoms along the axis of the molecule for the case in which the distances from the carbon atom to the two oxygen atoms are different. We recall that the vibrational state $\nu_1$ and $2\nu_2$ in the $CO_2$ molecule have approximately the same energy (a Fermi resonance), so that in practice each of these states is a mixture of states.

Gough and Miller[28] found the parameters in this expression for the ionization of the cluster CO · CO. In particular, at an energy of 100 eV they found the ratio of cross sections $\sigma_2/\sigma_1 = 2$. This result is not surprising, since the ionization in a van der Waals molecule occurs independently for each simple molecule. They also found $f = 0.85$, i.e., that only 15% of the ionizd van der Waals CO · CO molecules convert into $CO^+ \cdot CO$ cluster ions.

Since the equilibrium configurations of van der Waals molecules and the corresponding cluster ions are different, a substantial fraction of the cluster ions can be formed in long-lived unstable states upon electron-impact ionization of van der Waals molecules. The lifetimes of these states depend on the initial state of the van der Waals molecule and on the fields in the mass spectrometer. These problems have recently come under study.[29–33] We see that the mass-spectrometric method for finding the density of van der Waals molecules must be used carefully and cautiously.

## 4. FORMATION AND DECAY OF VAN DER WAALS MOLECULES

The rate at which van der Waals molecules form and break up in gases is of particular interest, since these processes determine the rate at which clusters form in gases, and these clusters may nucleate the appearance of a new phase. For this reason, these processes have attracted interest for a long time now (see, for example, Refs. 34, 44, 132–134). Recent progress in this field has been made by taking advantage of new computational capabilities. The rates at which van der Waals molecules form and break up are calculated by the Monte Carlo method with the real interaction parameters of the colliding particles. Calculations of this type provide the greatest amount of information about the formation and breakup of van der Waals molecules, and we will accordingly take a closer look at them.

The basic thrust of the research on the formation and breakup of van der Waals molecules is at present to study the simplest inert gas molecules. We will accordingly discuss the processes involved and then look at the corresponding results. The formation and breakup of the simplest inert gas molecules—dimers— occur in accordance with

$$3A \underset{k}{\overset{\mathscr{K}}{\rightleftarrows}} A_2 + A. \tag{3}$$

The rate constant $\mathscr{K}$ of the three-body formation of van der Waals molecules $A_2$ —dimers— and the rate constant ($k$) for their breakup in collisions with atoms are related by

$$k = K_{eq} \cdot \mathscr{K}. \tag{4}$$

If the dissociation energy ($D$) of van der Waals molecule $A_2$ is considerably larger than the thermal energy $T$, but if the vibrational quantum ($\hbar\omega$) of the molecule is small ($\hbar\omega \ll T$), the equilibrium constant $K_{eq}$ for process (3) is [34]

$$K_{eq} = \frac{1}{(2)\,4\pi r_m^2} \sqrt{\frac{M\omega^2}{\pi T}}\, e^{-D/T}, \tag{5}$$

where (2) is 2 if the nuclei are identical isotopes, or it is 1 if they are different isotopes. Here $r_m$ is the equilibrium distance between the nuclei in the molecule, and $M$ is the mass

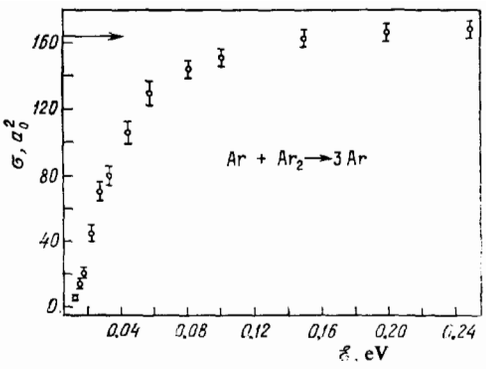


FIG. 3. Cross section for the breakup of an $Ar_2$ molecule in a collision with an argon atom according to a Monte Carlo calculation.[41] The arrow shows the geometric cross section of the molecule, i.e., $\pi r_m^2$, where $r_m$ is the distance between the nuclei in the $Ar_2$ molecule.

of a nucleus. It follows from (4) and (5) that if we know the rate constant for the two-body breakup of the van der Waals molecule in a collision with an atom we can also determine the rate constant for the three-body formation of the van der Waals molecule in the gas. We will thus restrict the discussion below to the breakup of a van der Waals molecule in a binary collision.

The breakup of van der Waals molecules of inert gases in binary collisions lends itself quite well to calculations.[35–42] The interaction potential of the colliding particles consists of the binary interaction potentials for the interactions between the individual atoms, and these potentials are well known. Furthermore, the motion of the nuclei can be described by the classical laws. Theoretical calculations can thus give us all the information we need. Corresponding calculations by the Monte Carlo method were carried out in Refs. 35–42. Figure 3 shows the dependence of the cross section for the reaction $Ar + Ar_2 \rightarrow 3Ar$ on the relative collision energy. The threshold energy, equal to the dissociation energy of the $Ar_2$ molecule, is 0.012 eV. We see from Fig. 3 that the cross section reaches saturation at energies slightly above the threshold. The cross section for the breakup of the dimer in the case of large molecules is approximately equal to the cross-sectional area of the dimer, $\pi r_m^2$ ($r_m$ is the equilibrium distance between the nuclei), marked by the arrow in Fig. 3.

Figure 4 shows the rate constant for the reactions $A_2 + A \rightarrow 3A$, where A is an inert gas atom, for a Maxwellian velocity distribution of the particles. If the dissociation energy of the van der Waals molecule satisfies $D \ll T$, then the rate constant for this process is $k_{max} \sim \bar{v}\sigma$, where $\bar{v}$ is the thermal velocity of the molecules, and $\sigma$ is the gaskinetic cross section. It follows that $k_{max} \sim 10^{-11}$–$10^{-10}$ cm$^3$/s. At thermal energies the calculated rate constants are considerably lower, close to $10^{-12}$ cm$^3$/s for the various inert gases. It follows from these calculations that for the various inert gases the rate constants for the reactions $A + A_2 \rightarrow 3A$ can be approximated well in the temperature range 200–400 K by

$$k(T) = k_0 \left(\frac{300}{T}\right)^{1/3}, \tag{6}$$

where $T$ is the temperature in kelvins. Table V shows values

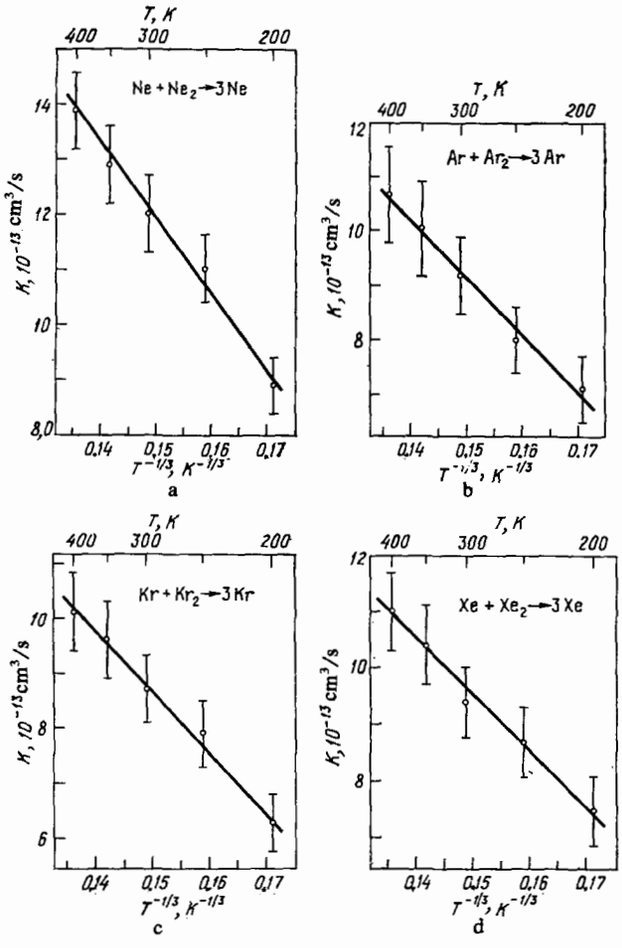


FIG. 4. Rate constant for the breakup of a dimer molecule of an inert gas in a collision with an atom of the same species.[41] a—Neon; b—argon; c—krypton; d—xenon. The indicated error is the statistical error of the Monte Carlo method.

of the parameter $k_0$ reconstructed from the calculations of Ref. 41.

Another interesting process is the collision of two van der Waals molecules. Figure 5 shows the rate constants for binary collisions of two dimers of an inert gas:

$$2Ar_2 \begin{cases} \longrightarrow Ar_3 + Ar, & (7a) \\ \longrightarrow Ar_2 + 2Ar, & (7b) \\ \longrightarrow 4Ar. & (7c) \end{cases}$$

With increasing temperature, the rate constant for the breakup of the dimers is seen to increase, while the rate constant for the exchange of an atom, (7a), falls off with increasing temperature. The calculation error indicated in Fig. 5 corresponds to the statistical error of the Monte Carlo method used for these calculations.[42]

TABLE V.

| A | Ne | Ar | Kr | Xe |
|---|---|---|---|---|
| $k_0$, $10^{-12}$ cm$^3$/s | 1.2 | 0.92 | 0.86 | 0.96 |

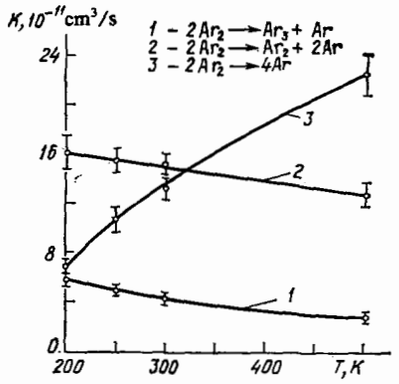


FIG. 5. Rate constant for the collision of two dimer argon molecules.[42]

## 5. ROTATIONAL SPECTRUM OF VAN DER WAALS MOLECULES

The study of the rf and microwave spectra constitutes a distinct area in research on van der Waals molecules. These spectra correspond to transitions between rotational states of molecules, and the clusters themselves usually consist of a dipole molecule and an inert gas atom. Rotational transitions occur quite intensely in a dipole molecule, and the resulting bond with the inert gas atom changes the parameters of these transitions slightly. By finding these parameters for the van der Waals molecules of interest with various isotopes of the atoms and also in an external electric field, one can ultimately determine the geometry of the molecule.

Consequently, research on the spectra of van der Waals molecules is somewhat distinct from other aspects of the research on neutral clusters. This research deals with some rather special entities which have received little study by other methods. Furthermore, information on such entities, which reduces primarily to information on the geometric properties of the molecule, is also different from the information found on van der Waals molecules by other methods.

We should begin our analysis of these processes with the study by Novick *et al.*,[45] who measured a high-resolution spectrum for the cluster Ar · HCl by the method of molecular beam electric resonance spectroscopy. This method with appropriate modifications has subsequently been used to record the spectra and reconstruct the properties of a long list of similar clusters. Table VI shows the parameters of van der Waals molecules of this type derived from these experiments.

The general idea of these experiments can be summarized as follows. An inert gas with a small admixture of dipole molecules is released into vacuum through a nozzle. Van der Waals molecules form in the low-temperature gas jet emerging from the nozzle. The jet passes through a spectrometer, where the absorption is measured as a function of the signal frequency in a narrow band of the rf or microwave spectrum. Spectrometers of various designs can be used, but certain fundamental elements will generally be present. Figure 6 shows a typical absorption spectrum[52] in the resonance region for the $2 \rightarrow 1 (J' \rightarrow J)$ transition of the Ar · $D^{81}Br$ molecule. The level splitting in this case results from an interaction of the total angular momentum of the molecule, which

TABLE VI. Parameters of van der Waals molecules* consisting of an inert gas atom and a hydrogen-halogen dipole molecule according to an analysis of the rotational spectra of these molecules.

| Molecule | $R_0$, Å | $R$, Å | $\theta$, deg | $\omega_s$, $cm^{-1}$ | Dipole moment, D | Binding energy meV | Reference |
|---|---|---|---|---|---|---|---|
| Ne·D$^{35}$Cl | 3.7906 | 3.838 | 65.0 **) | 21.9 | 0.4751 | 6.4 | 46 |
| Ar·HF | 3.5095 | 3.5466 | 41.04 | 42.2 | 1.335 | 14 | 47, 48 |
| Ar·DF | — | 3.4605 | 33.02 | 45.6 | 1.677 | — | 48 |
| Ar·H$^{35}$Cl | 3.9795 | 4.0088 | 41.60 | 32.4 | 0.8117 | 16 (23) | 45, 49–51 |
| Ar·D$^{35}$Cl | 3.976 | 4.025 | 33.7 | 34.4 | 1.0096 | 16 | 45,49–51 |
| Ar·H$^{79}$Br | 4.1331 | 4.1483 | 42.17 | 22.0 | 0.5742 | 11 (25) | 52, 57 |
| Ar·D$^{79}$Br | 4.1529 | 4.1747 | 34.38 | 25.9 | 0.7563 | 16 | 52, 57 |
| Ar·$^{35}$ClF | — | 3.300 | 8.7 | 47.2 | 1.053 | 28 | 53 |
| $^{84}$Kr·H$^{35}$Cl | — | 4.1106 | 37.75 **) | 32.29 | 0.9567 | 22 (30) | 55, 56 |
| $^{84}$Kr·D$^{35}$Cl | — | 4.1251 | 30.54 **) | 32.62 | 1.1064 | 19 | 55, 56 |
| $^{84}$Kr·H$^{79}$Br | — | 4.2572 | 38.03 **) | 23.4 | — | 20 (31) | 57 |
| $^{84}$Kr·D$^{79}$Br | — | 4.2809 | 31.00 **) | 25.0 | — | 24 | 57 |
| $^{84}$Kr·$^{35}$ClF | | 3.388 | 8.11 | 43.6 | 1.136 | 36 | 49 |
| $^{129}$Xe·HF | 3.7772 | 3.8152 | 35.55 | 45 | 1.7359 | — | 58 |
| $^{129}$Xe·DF | 3.7339 | 3.8111 | 29.4 | 47 | 1.9537 | — | 58 |
| $^{129}$Xe·H$^{35}$Cl | 4.275 | 4.246 | 34.8 | 33.9 | 1.0901 | 37 | 59, 60 |
| $^{129}$Xe·D$^{35}$Cl | 4.288 | 4.258 | 28.2 | 34.8 | — | 24 | 60 |

*$R_0$ is the distance from the inert gas atom to the center of mass of the dipole molecule; $R$ is the distance from the inert gas atom to the halogen atom; $\theta$ is the angle between the axis of the dipole molecule and the line connecting the center of mass of the dipole molecule to the nucleus of the inert gas atom; $\omega_s$ is the vibration frequency in the direction of the weak bond, and $\mu$ is the dipole moment of the molecule.

**This is the angle formed by the hydrogen atom, the halogen atom, and the inert gas atom.

consists of the rotation or angular momentum of the molecule and the nuclear spin of the bromine atom, with the internal field of the molecule, which is caused by the presence of the argon atom. The states of the molecule accordingly lose their degeneracy in the component of the total angular momentum, and the resonances in Fig. 6 correspond to transitions between states with different components of the total angular momentum.

The capabilities of this method stem from the high quality factor of the resonators in the rf and microwave regions. When there are van der Waals molecules in a resonator, and these molecules absorb at the resonant frequency, the quality factor of the resonator is reduced. By measuring the frequency characteristics of a resonator while a gas jet with van der Waals molecules passes through it one can thus measure the absorption spectrum of these molecules. In practice the spectral resolution of these measurements is of the order of $10^{-6}$ (this is the ratio of the resolution of the instrument to the signal frequency).

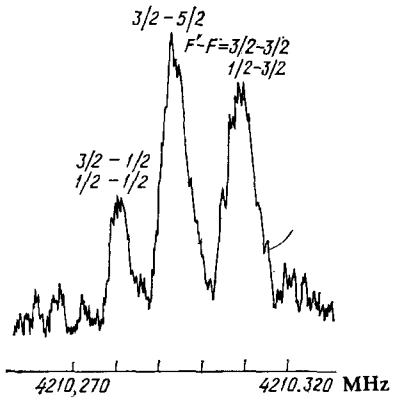


FIG. 6. A part of the rotational spectrum of Ar · D$^{81}$Br recorded[52] with a high resolution for the rotational transition $1 \rightarrow 2 (J \rightarrow J')$ and for a change in the angular momentum, $F_1$, which is composed of the rotational angular momentum and the spin of the bromine atom, $3.2 \rightarrow 1/2$ (the nuclear spin of $^{81}$Br is 3/2). The hyperfine structure of this transition results from the quadrupole interaction of the spin of the deuterium nucleus (spin 1) with the rotation of the molecule. The resonances correspond to transitions with various values of the total angular momentum $F$, which is composed of the angular momentum $F_1$ and the spin of the deuterium.

Consequently, high-resolution recordings of the rotational spectra of the van der Waals molecules of interest provide information on the interaction in these molecules due to the presence of the internal field of the inert gas atom. This information on the rotational spectrum of the molecules includes information on the various transition rotational angular momenta and the various isotopes of the atoms in the molecule. Armed with all this information one can reconstruct certain parameters of the van der Waals molecule, at the very least its configuration. The analysis of the data is simplified further by the circumstance that the rotational temperature of the molecules in the beam is low (tens of kelvins), so that the number of possible rotational transitions is severely limited.

Table VI shows some results obtained by this method. These are results on the configuration of the molecules; they give the spatial positions of the nuclei in the molecule, the dipole moment of the molecule, and the frequency ($\omega_s$) of the vibrations along the axis connecting the inert gas atom to the dipole molecule. This vibration frequency is reconstructed from the dependence of the rotational constant on the rotational angular momentum.

In addition to measurements of these pieces of information about the rotational spectra of the molecules, it is common to find measurements of the level splitting of the molecules in a static electric field. This splitting provides further

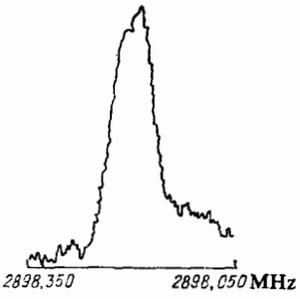


FIG. 7. Resonance for the transition of the Ar · $^{32}SO_3$ molecule with $K$, $K' = 0$, $J = 0$, $J' = 1$ in a static electric field of 100/48 V/cm (Ref. 61).

information on the spectrum of the molecules and leads to a reliable reconstruction of the parameters of interest of the van der Waals molecules. Figure 7 shows a representative resonance in the rotational spectrum of the Ar · $O_3$ molecule in an electric field. Although it might appear that a study of the rotational spectrum of molecules in an external electric field would provide new information on the structure of the van der Waals molecule, in practice the dependence of the spectrum on the external field is not included in the results which are analyzed; instead, the Stark effect is used to "overwhelm" the unwanted interactions to simplify the analysis of the results. The volume and reliability of the data obtained by the Stark-effect method are thus similar to those of the data found from the spectra of noninteracting van der Waals molecules.

These measurements are pertinent to van der Waals molecules of a special type, which include a dipole molecule or a molecule which actively absorbs in the rf or microwave frequency range. Measurements of this type therefore provide information on the structure of such molecules which so far does not overlap with the results of other approaches.

An important question in the analysis of these molecules is the type of bond in molecules which include dipole molecules. Although we call these entities "van der Waals molecules," it has been pointed out in many places (see Ref. 54, for example) that an ion-ion bond may play an important role in them. To illustrate this question we show in Tables VII and VIII the distance between the nearest atoms in the weak bond for two types of molecules. In molecules of the Ar-HX type, where X is a halogen atom, the distance between the argon atom and the hydrogen (or deuterium) atom remains the same within 5% for various compounds, indicating that the interaction of the particles in these molecules is of a van der Waals nature.

An interaction of a different type occurs in van der Waals molecules in which an argon atom is a weakly bound neutral atom, and the negative charge in the dipole molecule is concentrated at the sulfur atom. In these molecules the weak bond is the Ar-S bond; i.e., the sulfur atom is the nearest neighbor of the argon atom. If the weak bond in these molecules were determined only by the interaction of the argon atom with the atom nearest it—the sulfur atom—then these distances would be approximately the same for the various molecules of this type. We see from Table VIII that the interaction of the argon atom with the dipole moment of the molecule plays an important role in the formation of the weak bond in the molecules listed there; as a result, there is a slight redistribution of the charge in the molecule.

Calculations confirm that the dopole moment of the molecule plays a role in the formation of the bond for these van der Waals molecules. Benzel and Dykstra,[69] for example, have carried out calculations on the interaction of the $N_2$ · HF, CO · HF, and HCN · HF van der Waals molecules, whose configurations had been determined earlier in the experiments of Refs. 82, 106, and 107, respectively. The calculations showed that the formation of the complex is governed primarily by the electrostatic interaction between the electric moments of the molecules. In the case of the $N_2$ · HF molecule, for example, the energy of the interaction of the dipole moment of the HF molecule with the quadrupole moment of the $N_2$ molecule in the comlex is 40 meV, while the bond rupture energy—the total energy of the attraction between the fragments in the complex—is 98 meV. We might note that the bond rupture energy of this molecule is considerably higher than those of the simplest van der Waals molecules (cf. Tables I–III).

Yet another example of this type for clusters including an argon atom and a linear triatomic molecule is shown in Table IX. Although the molecules in these clusters may not have a dipole moment in their free state, these molecules are optically active in the rf and microwave frequency ranges and thus suitable for experiments by this method. They are particularly attractive for this purpose because the optical activity of these van der Waals molecules is intensified by the interaction in them, which causes some redistribution of charge.

It follows from Table IX that the configuration of the molecules listed here and the parameters of the molecules themselves are not greatly different. It follows that a van der Waals interaction plays a leading role in the formation of the weak bond in these molecules.

This method of studying van der Waals molecules, by means of high-resolution measurements of the spectra of the molecules in the rf and microwave frequency ranges, was originally used to study clusters consisting of atoms and diatomic dipole molecules. The method was later extended to a long list of van der Waals molecules which are optically ac-

TABLE VII. Distance between the argon atom and the hydrogen atom (or the deuterium atom) in the Ar · HX (or Ar · DX) molecule (X is a halogen atom)[45,48,50,52,57]

| Molecule | Ar·HF | Ar·DF | Ar·HCl | Ar·DCl | Ar·HBr | Ar·DBr |
|---|---|---|---|---|---|---|
| $R$, Å | 2.630 | 2.626 | 2.732 | 2.755 | 2,727 | 2.767 |

TABLE VIII. Distance between the argon atom and the sulfur atom in the corresponding van der Waals molecules.

| Molecule | Ar·$H_2S$ | Ar·OCS | Ar·$SO_2$ | Ar·$SO_3$ |
|---|---|---|---|---|
| Distance Ar—S, Å | 3.99 | 4.10 | 3.66 | 3.35 |
| Reference | 63 | 64 | 61, 63 | 63 |

tive in this part of the spectrum.

A topic of particular interest is the bond rupture energy in a van der Waals molecule. Molecular-beam electric resonance spectroscopy can reveal the configuration of the molecule and the vibration frequencies of weak bonds. This information can be used along with a specified interaction potential between the fragments of the molecule to determine the dissociation energy of the molecule. The potential of the interaction between the components of a van der Waals molecule is customarily written as a Lennard-Jones potential. Although this is not the correct potential, this approach does give a correct estimate of the depth of the interaction potential of the fragments in the van der Waals molecule. Table VI lists these values for several van der Waals molecules. These values were found by this method in studies of the corresponding van der Waals molecules. The discrepancies between the results of certain studies are evidence of imperfections in the calculations, since the parameter values are the same or nearly so.

Unfortunately, the information of the type discussed above has almost no overlap with the data obtained by other methods. An exceptional case is the Ar · HCl molecule, for which the depth of the potential well in the interaction between its components was determined in Ref. 62 from differential cross sections for the scattering of argon atoms by HCl molecules at a relative collision energy of 88 meV. The depth found for the well in the interaction potential was 16 meV, in agreement with the data in Table II. The rupture enthalpys of the weak bonds (Section 3) were determined in Refs. 26 and 27 from measurements of the equilibrium constants for the Ar · HCl and Ar · HBr molecules; these enthalpys are $-53$ and $-46$ meV, respectively. The magnitudes of these enthalpys can be identified within the thermal energy with the rupture energies of the corresponding bonds. Since the rupture energies of these bonds are comparable to the thermal energy of the particles, however, the discrepancy between the rupture enthalpys of these bonds and their rupture energies (Table VI) tells us nothing.

The data in Table X give an idea of the nature of the binding in these van der Waals molecules. Table X lists the dipole moments of the molecules in clusters according to Refs. 69 and 70, along with the measured dipole moment of the cluster itself or the projections of the dipole moment onto the rotation axes of the cluster ($\mu_a$, $\mu_b$, and $\mu_c$). We see from this table that a slight redistribution of charge may accompany the formation of the weak bond in these van der Waals molecules. As a result of this redistribution, the cluster may acquire a small dipole moment even if the dipole moment of its components is zero. This is what happens in the cases of Ar · $CO_2$, Ar · $BF_3$, and Ar · $C_2H_2$, among others. Where a bond is formed by a molecule which has an initial dipole moment, this dipole moment will change slightly and will be reoriented. It can thus be concluded that the formation of the bond in van der Waals molecules of this type is accompanied by a slight charge redistribution, which may affect the magnitude of the binding. Even if this redistribution is slight, the method is sensitive enough to detect it.

Molecular-beam electric resonance spectroscopy, with its capability of providing a high-resolution rotational spectrum of molecules, is thus an informative tool for studying cluster molecules. This method was originally used for van der Waals molecules including an inert gas atom and a diatomic dipole molecule, and it was later used for different groups of molecules exhibiting optical activity in the rf and microwave ranges. This method has provided a great deal of information about the configuration of these molecules and on the parameters of the vibrations associated with the weak bond. Analysis of the results provided by this method leads to the conclusion that a redistribution of charge due to an interaction can play a role in the formation of the weak bond in these molecules.

A few measurements of the interaction parameters in van der Waals molecules and of the parameters of the collisions of these molecules with buffer particles have been carried out through the use of magnetic methods to produce a gas jet with van der Waals molecules having a specified rotational angular momentum (see Refs. 128–131, for example). Among the molecules which have been studied is the hydrogen molecule, which exhibits the strongest interaction with a magnetic field. As an example we will discuss the experimental approach of Ref. 131, where the hyperfine structure of $H_2$–X van der Waals molecules ($X \equiv$Ne, Ar, Kr) was measured (Fig. 8). A gas jet containing these van der Waals mole-

TABLE IX. Parameters of van der Waals molecules consisting of an argon atom and a linear triatomic molecule.

| Molecule | $R_0$, Å | θ, deg | $\omega_s$, $cm^{-1}$ | $\omega_b$, $cm^{-1}$ | Reference |
|---|---|---|---|---|---|
| Ar·$CO_2$ | 3.493 | 82.5 | 37.5 | 38.9 | 65 |
| Ar·$^{14}N_2O$ | 3.470 | 81.4 | 39.4 | 45.8 | 66 |
| Ar·$^{15}N_2O$ | 3.466 | 81.8 | 39.1 | 44.5 | 66 |
| Ar·OCS | 3.578 | 81.9 | — | — | 64 |

*$R_0$ is the distance from the argon atom to the central atom of the triatomic molecule; $\theta$ is the angle between this direction and the axis of the triatomic molecule; $\omega_s$ is the vibration frequency along the direction of the weak bond; and $\omega_b$ is the vibrational frequency in the perpendicular direction.

TABLE X. Dipole moments of van der Waals molecules.

| Molecule | Dipole moment of constituent molecule, D | Dipole moment of cluster, D | Components of the dipole moment of the cluster, D | Reference |
|---|---|---|---|---|
| $Ar \cdot CO_2$ | 0 | 0.0679 | — | 65 |
| $Ar \cdot H_2S$ | 0.974 | — | $\mu_a = 0,186$<br>$(\mu_a^2 + \mu_c^2)^{1/2} = 0,8$ | 75 |
| $Ar \cdot {}^{15}N_2O$ | 0.1609 | — | $\mu_a = 0.0421$<br>$\mu_b = 0.141$ | 66 |
| $Ar \cdot O_3$ | 0.5337 | — | $\mu_a = 0.1010$<br>$\mu_b = 0$<br>$\mu_c = 0.4643$ | 71 |
| $Ar \cdot OCS$ | 0.7152 | — | $\mu_a = 0,215$<br>$\mu_b = 0.669$ | 64 |
| $Ar \cdot SO_2$ | 1.633 | — | $\mu_a = 0.2674$, $\mu_b = 0$<br>$\mu_c = 1.465$ | 61 |
| $Ar \cdot BF_3$ | 0 | 0.176 | — | 72 |
| $Ar \cdot C_2H_2$ | 0 | 0.270 | — | 73 |
| $Ar \cdot C_2D_2$ | 0 | 0.270 | — | 73 |
| $Ar \cdot SO_3$ | 0 | 0.268 | — | 63 |
| $Kr \cdot SO_3$ | 0 | 0.369 | — | 74 |
| $N_2 \cdot BF_3$ | 0 | 0.35 | — | 72 |
| $N_2 \cdot O_3$ | 0 | 0.46 | — | 63 |
| CO—HF | 1.827 | 2.36 | — | 69 |
| $(HF)_2$ | 1.827 | — | $\mu_a = 2,987$ | 76 |
| $(DF)_2$ | 1.820 | — | $\mu_a = 2.9919$ | 76 |
| HF·DF | 1.827<br>1.820 | — | $\mu_a = 3.029$ | 76 |
| $HF \cdot H^{35}Cl$ | 1.827<br>1.108 | — | $\mu_a = 2.4095$ | 77 |
| $HF \cdot D^{35}Cl$ | 1.827<br>1.103 | — | $\mu_a = 2.483$ | 77 |
| $N_2$—HF | 1.227 | 8.47 | — | 69 |
| HF—HCN | 1.227<br>2.985 | 5.59 | — | 80, 82 |
| $CO_2 \cdot HF$ | 1.827 | 2.2465 | — | 67 |
| $CO_2 \cdot DF$ | 1.820 | 2.3024 | — | 67 |
| $N_2O \cdot HF$ | 0.1609<br>1.827 | — | $\mu_a = 2.069$<br>$\mu_b = 0.69$ | 68 |
| $N_2O \cdot DF$ | 0.1609<br>1.820 | — | $\mu_a = 2.125$<br>$\mu_b = 0.63$ | 68 |
| $(H_2O)_2$ | 1.85 | 2.60 | | 79, 81 |
| $BF_3 \cdot CO$ | 0.1098 | 0.592 | — | 72 |

cules emerges from a nozzle and is shaped into a narrow beam by a skimmer. This beam passes through a Rabi magnet with a nonuniform field; this magnet singles out a beam of molecules with specified magnetic quantum numbers. This beam then enters an rf radiation zone, where the magnetic state of the molecule can be changed. After passing through this zone, the beam enters another Rabi magnet, which singles out the molecules with the other magnetic moment. The beam is then ionized, and the molecules are converted into cluster ions, which are detected by a quadrupole mass spectrometer.

In this experimental approach one can tune the Rabi magnets to various magnetic states of the van der Waals molecules, and by varying the frequency of the rf signal one can determine which resonant frequency corresponds to these transitions. In this manner one can reconstruct the spectrum of transitions between the hyperfine structure states of these van der Waals molecules, and from this spectrum one can determine the details of the interaction potential of the components of the van der Waals molecules. This method provides detailed information on the interaction potential which does not overlap with the results obtained by other approaches. Although there have been only a few studies of the parameters of van der Waals molecules by magnetic methods, these methods have some interesting possibilities and may make an important contribution to the information available on van der Waals molecules.

## 6. PHOTOIONIZATION OF VAN DER WAALS MOLECULES

Although experiments on the photoionization of van der Waals molecules were begun only a few years ago, some

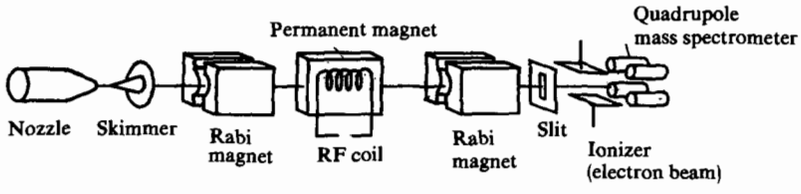


FIG. 8. Experimental arrangement for measuring the hyperfine structure of van der Waals molecules.

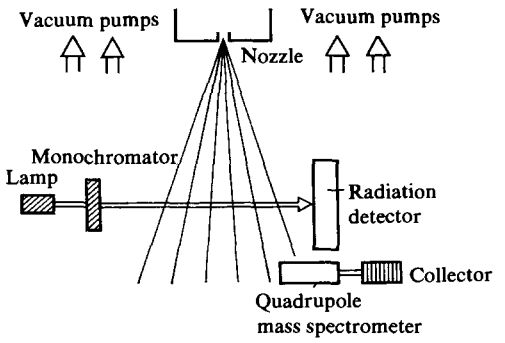


FIG. 9. Experimental arrangement for studying the photoionization of van der Waals molecules.

important results have been established. The idea of these experiments is to illuminate a gas flow with monochromatic vacuum-UV radiation and simultaneously measure the current of molecular ions of a given species formed by this radiation. This measurement method requires that the dimensions of the quadrupole mass spectrometer be small, since the spectrometer must be put in the chamber with the gas flow. This is a typical example of the present state of atomic physics, where refinements and modifications of experimental apparatus are opening up some new experimental approaches and are yielding fundamentally new information.

Figure 9 shows the basic arrangement for measurements of the photoionization of van der Waals molecules. The van der Waals molecules are formed during adiabatic cooling in a supersonic gas jet emerging from a nozzle into vacuum. A low pressure maintained by differential pumping in the chamber which the jet enters. The jet is irradiated by a capillary discharge lamp, which emits either a hydrogen pseudocontinuum over the interval 900–1600 Å or a Hopfield continuum in helium over the interval 650–900 Å. The radiation passes through a monochromator, and the gas jet is bombarded by monochromatic radiation with a line width as small as [2] ~0.1 Å in the best measurements.

As the gas jet is bombarded by the monochromatic radiation, a quadrupole mass spectrometer measures the current of ions of a species of interest. Figure 10 shows a typical result.[98] We see that this method can reveal the relative cross section for the photoionization of van der Waals molecules accompanied by the formation of ions of a given species.

Table XI summarizes data found on the ionization potentials of van der Waals molecules by this method. These results are useful in several ways. In the first place, they constitute fundamental information on the properties of molecules. Second, a study of photoionization thresholds yields information about the binding energies in the ion complexes. These measurements have revealed the bond rupture energies of many complex and cluster ions. Third, these

[2] This quantity depends on the intensity of the radiation sources available in the given part of the spectrum. As an example we cite the characteristics of the source in Ref. 83, where the photoionization of $Ar_2$ was studied with a resolution of 0.3 Å. A capillary discharge lamp 40 cm long was triggered by a high-voltage pulsed discharge in helium. Near the maximum of the Hopfield continuum, at $\lambda \approx 820$ Å, this lamp produced $7 \cdot 10^9$ photons per second per angstrom.

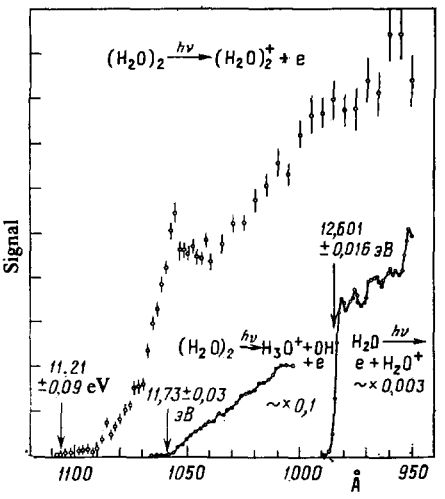


FIG. 10. Photocurrent of ions of particular species as a function of the wavelength of the ionizing radiation.[98]

TABLE XI. Ionization potentials of van der Waals molecules.

| Molecule | Ionization potential of molecule, eV | Ionization potential of component, eV | Reference |
|---|---|---|---|
| $Ar_2$ | 14.54±0.02 | 15.7597 | 84 |
| | 14.475±0.025 | » | 83 |
| NeAr | 15.685±0.004 | » | 85 |
| $Kr_2$ | 12.87±0.02 | 13.9997 | 84 |
| | 12.865±0.003 | | 86 |
| NeKr | 13.950±0.003 | » | 85 |
| ArKr | 13.425±0.020 | » | 87 |
| $Kr_3$ | 12.79±0.05 | » | 88 |
| $Kr_4$ | 12.76±0.04 | » | 88 |
| $Xe_2$ | 11.13±0.01 | 12.130 | 89 |
| NeXe | 12.094±0.004 | » | 85 |
| ArXe | 11.985±0.017 | » | 87 |
| KrXe | 11.757±0.017 | » | 87 |
| $Xe_3$ | 10.88±0.04 | » | 90 |
| $(CO)_2$ | 13.05±0.04 | 14.013 | 91 |
| $(CO)_3$ | 12.91±0.04 | » | 91 |
| $(HBr)_2$ | 10.83 | 11.66 | 92 |
| $(HCl)_2$ | 11.91 | 12.71 | 92 |
| $(N_2)_2$ | 14.69±0.05 | 15.58 | 91 |
| $(N_2)_3$ | 14.64±0.05 | » | 91 |
| $(NO)_2$ | 8.736±0.002 | 9.265 | 91 |
| $(NO)_3$ | 8.486±0.017 | » | 91 |
| $(NO)_4$ | 8.39±0.03 | » | 91 |
| $(NO)_5$ | 8.32±0.03 | » | 91 |
| $(NO)_6$ | 8.28±0.03 | » | 91 |
| $(O_2)_2$ | 11.66±0.03 | 12.07 | 93 |
| | 11.80±0.02 | » | 88 |
| $(O_2)_3$ | 11.72±0.02 | » | 88 |
| $(O_2)_4$ | 11.66±0.03 | » | 88 |
| $(O_2)_5$ | 11.60±0.04 | » | 88 |
| $(CO_2)_2$ | 13.32±0.02 | 13.79 | 94 |
| $(CO_2)_3$ | 13.24±0.02 | » | 94 |
| $(CO_2)_4$ | 13.18±0.02 | » | 94 |
| $(CS_2)_2$ | 9.63±0.03 | 10.068 | 95 |
| | 9.36±0.02 | » | 96 |
| $(CS_2)_3$ | 9.22±0.02 | » | 96 |
| $(CS_2)_4$ | 9.10±0.02 | » | 96 |
| $(CS_2)_5$ | 9.04±0.02 | » | 96 |
| $CS_2 \cdot OCS$ | 9.858±0.024 | » | 97 |
| $(H_2O)_2$ | 11.21±0.09 | 12.61 | 98 |
| $(H_2S)_2$ | 9.74±0.01 | 10.45 | 99 |
| $(H_2S)_3$ | 9.63±0.01 | » | 99 |
| $(H_2S)_4$ | 9.61±0.01 | » | 99 |
| $(H_2S)_5$ | 9.58±0.01 | » | 99 |
| $(H_2S)_6$ | 9.50±0.02 | » | 99 |
| $(H_2S)_7$ | 9.63±0.03 | » | 99 |
| $(N_2O)_2$ | 12.35±0.02 | 12.89 | 94 |
| $(OCS)_2$ | 10.456±0.026 | 11.174 | 97 |
| $(OCS)_3$ | 10.408±0.026 | » | 97 |
| $(SO_2)_2$ | 11.72±0.03 | 12.35 | 100 |
| $(NH_3)_2$ | 9.54±0.05 | 10.166 | 101 |
| $(C_2H_4)_2$ | 9.72±0.02 | 10.51 | 102 |
| $(C_2H_4)_3$ | 9.56±0.02 | » | 102 |

measurements show that the photoionization thresholds of van der Waals molecules are considerably lower than the ionization potentials of the components of these molecules. For this reason, the formation of van der Waals molecules in a gas may govern the photoionization of the gas in cases in which the wavelength of the light is slightly below the threshold for photoionization of the gas. In particular, we might expect the photoionization of oxygen van der Waals molecules to play a role in those layers of the atmosphere which do not transmit radiation with a wavelength shorter than 1027 Å but which do transmit at wavelengths shorter than 1050 Å. The photoionization of van der Waals molecules is more important for the atmospheres of planets lying farther than the earth from the sun.

The process itself by which van der Waals molecules undergo photoionization is a complicated one. This process gives rise to molecular and cluster ions whose binding energies are considerably higher than the binding energies of the van der Waals molecules. The equilibrium distances between the nuclei in these ions, when they are in their vibrational ground state, are thus considerably different from the equilibrium distances between the nuclei in the van der Waals molecules. It follows that the Franck-Condon factors for the photoionization of van der Waals molecules are small near the threshold. Correspondingly, the mechanism for photoionization near the threshold may involve the initial formation of various autoionization states of the van der Waals molecule, and the decay of these autoionization states may lead to the ionization of the van der Waals molecule. In this case, the dependence of the photoionization cross section on the photon energy should have a complicated oscillatory structure. Such structure can be seen in high-resolution measurements, and it complicates the accurate determination of thresholds. Figure 11 shows an example of the situation, for the particular case of the photoionization of the NeAr molecule. We see that the irregular oscillatory structure in the cross section is evidence that various types of autoionization states are involved in the process.

This circumstance, which is related to the difference between the equilibrium configurations of the van der Waals molecule and of the corresponding cluster ion, is demonstrated by Table XII, which shows the diabatic ionization potential (i.e., without a change in the configuration of the nuclei) and the adiabatic ionization potential of cluster molecules of xenon.[103,104] If the photon energy exceeds the diabatic ionization potential, the configuration of the nuclei will

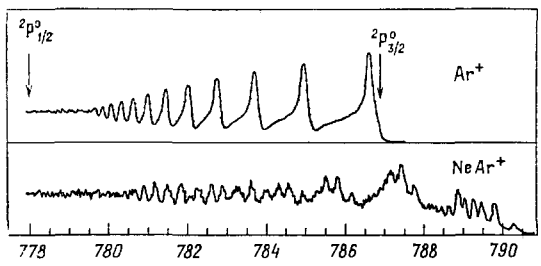


FIG. 11. Relative photoionization cross section of the argon atom and the NeAr van der Waals molecule near the threshold.[85]

TABLE XII.

| System | Ionization potential, eV | |
|---|---|---|
| | Diabatic | Adiabatic |
| $Xe_2$ | 11.76±0.01 | 11.13±0.01 |
| $Xe_3$ | 11.30±0.05 | 10.88±0.04 |
| Solid xenon | 9.7 | 9.7 |

remain basically the same upon the transition, and the oscillatory nature of the photoionization cross section will cease to dominate the situation.

To conclude this section we note that research on the photoionization of van der Waals molecules, which has been carried out in accordance with a master plan and which has been directed primarily toward the behavior of the cross sections near the thresholds, has yielded a rich store of information on the ionization potentials of van der Waals molecules and also on the dissociation energies of the molecular and cluster ions formed in the process. The threshold measurements in experiments on the photoionization of clusters are much more accurate than those from experiments on electron-impact ionization of clusters (see Ref. 105, for example).

## 7. PHOTODISSOCIATION OF VAN DER WAALS MOLECULES

The photodissociation of van der Waals molecules whose components are molecules has been the subject of extensive research. In this case there is a photoexcitation of one of the molecules in the cluster, and the excitation energy exceeds the energy required to rupture the weak bond of the van der Waals molecule. The excited molecule which is formed quickly dissociates, decaying into its components. Research in this field began with the study by Klemperer,[108] who excited the $(HF)_2$ molecule near the vibrational transition of the HF molecule. The dissociation time of the excited $(HF)_2$ molecule was $5 \cdot 10^{-11}$ s; i.e., the vibrational excitation—an extremely effective process—of one of the components of the molecule automatically results in a subsequent dissociation of the molecule.

The early research on the photodissociation of van der Waals molecules centered around experiments on many-photon dissociation, which were oriented toward the development of laser methods for isotope separation. It has been stated (see Ref. 109, for example) that since the dissociation energy of van der Waals molecules is relatively low their photodissociation is much more efficient than that of other polyatomic molecules, so that they are convenient for use in isotope separation. This assertion is extremely problematical, because severe difficulties arise in attempts to separate the monomers of the molecules from their van der Waals molecules. As a result, at present one should not seriously consider the photodissociation of van der Waals molecules as a method for isotope separation, but it is still worthwhile to analyze the scientific aspect of the research on this process.

The absorption spectrum of a van der Waals molecule is

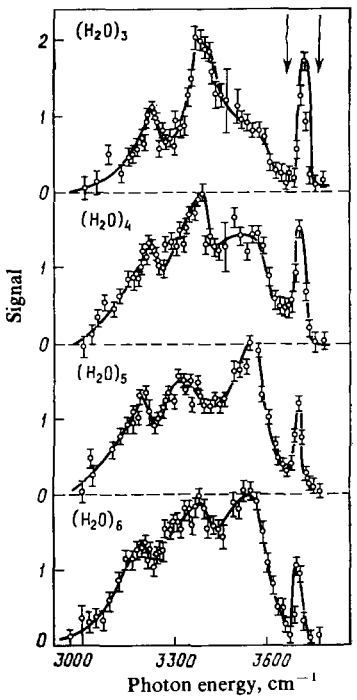


FIG. 12. Absorption spectrum of $(H_2O)_n$ van der Waals molecules before the threshold for excitation of the hydrogen bond.[109] The arrows show the absorption lines $\nu_1$ and $\nu_3$ of the water molecule which are responsible for the excitation of the hydrogen bond.

the shifted and broadened absorption spectrum of its components. The rotational degrees of freedom of the simple molecules are frozen in this spectrum, while the lines of the fundamental vibrational transitions are shifted slightly and broadened in a complicated way by the interaction. The shifts of the centers of the lines are relatively small, but they distinguish the parts of the spectrum where simple and cluster molecules absorb. We have already seen one example of the absorption spectra of simple and cluster molecules (Table IV); another example is shown in Fig. 12, which contains the absorption spectra of water molecules.[109] The part of the spectrum shown in Fig. 12 corresponds to the excitation of hydrogen bonds. In the water molecule, the frequencies corresponding to this vibration are $\nu_1 = 3657\ cm^{-1}$ and $\nu_3 = 3756\ cm^{-1}$. The resonance at the right in thise spectra apparently corresponds to the $\nu_1$ vibration in the isolated molecule. In clusters, the various vibrations interact, giving rise to the broadening of the absorption spectrum. The absorption spectrum shown in Fig. 12 for cluster water molecules is near $2\nu_2$ ($\nu_2 = 1595\ cm^{-1}$ is a vibration of the water molecule) and apparently corresponds to an interaction of the $2\nu_2$ and $\nu_1$ vibrations for interacting water molecules. We see that the absorption resonance at the frequency $\nu_1$ for the isolated water molecule decreases as the cluster becomes more complicated.

The standard way of measuring the absorption spectra of van der Waals molecules can be outlined as follows. The van der Waals molecules are formed in a gas jet emerging from a nozzle. The relative absorption of radiation by this jet is measured in some part of the spectrum near vibrational transitions of the fragment molecules of the van der Waals molecules. The information found on the resonances in the absorption spectrum in this manner is used to select the strongest transitions in the system. The particular particles responsible for the absorption at the corresponding lines in the spectrum are identified by simultaneously measuring the current of the ions of a particular species which is produced when part of the jet flows through a quadrupole mass spectrometer after a partial ionization of the jet. Measurements of this current with the laser turned on and off reveal which molecules are absorbing at the given transition.

To explain this method further we consider a specific example. Geraedts[119] studied the absorption of a jet of sulfur hexafluoride emerging from a nozzle near the resonance lines of $SF_6$ in the interval 920–970 $cm^{-1}$. It was found that the application of a laser beam at 938 $cm^{-1}$ and 960 $cm^{-1}$ reduces the current of $SF_5^+ \cdot SF_6$ ions, by about 53% at a laser power density of 140 $W/cm^2$ under those experimental conditions. This result is evidence that the laser beam at this frequency is absorbed by $(SF_6)_2$ molecules, which give rise to the current $SF_5^+ \cdot SF_6$ ions. Under those experimental conditions, roughly half these molecules are broken up by absorption of the laser beam.

The excitation of the components of a van der Waals molecule ultimately leads to its decay; the predissociation time is an important parameter of the process. The predissociation time of a van der Waals molecule is reflected in the shape of the photodissociation spectrum, i.e., the dependence of the absorption coefficient on the photon wavelength near the resonance. By analyzing this dependence we can determine the predissociation time. Table XIII shows the predissociation times found[110] in this manner for van der Waals molecules containing the $C_2H_2$ molecule. In this case, the $\nu_7$ vibration is excited in the $C_2H_2$ molecule; the excitation energy of this vibration is near 950 $cm^{-1}$. It can be seen from Table XIII that the predissociation times of the various van der Waals molecules are not greatly different; the similarity stems from the identical nature of the energy transfer from this vibration to the weak bond in the various cases. The average statistical value of the predissociation time for these molecules and the excited bond is $(5 \pm 2) \cdot 10^{-13}$s. This is a relatively short time, implying that the interaction between the excited vibration and the weak bond is quite strong. Furthermore, since this time is short it can be found by analyzing the curve of the photodissociation spectrum.

Figure 13 shows the predissociation time calculated[111] for the $N_2O(001) \cdot N_2O$ molecule, which is structurally similar to the $(CO_2)_2$ molecule discussed above. The decay time of

TABLE XIII.

| Van der Waals molecule | Position of absorption peak, $cm^{-1}$ | Predissociation time, $10^{-12}$s |
|---|---|---|
| $(C_2H_2)_2$ | 952.3±0,5 | 0.44±0,05 |
| $(C_2H_2)_3$ | 952.3±0,5 | 0.50±0,07 |
| $(C_2H_2)_5$ | 953.2±0,9 | 0.33±0,05 |
| $(C_2H_2)_7$ | 953.2±0,9 | 0.33±0,05 |
| $Ar \cdot C_2H_4$ | 950.0±0,5 | 0.59±0,13 |
| $Kr \cdot C_2H_4$ | 949.1±0,7 | 0.55±0,14 |
| $C_2F_4 \cdot C_2H_4$ | 954,7±0,2 | 0.89±0,10 |

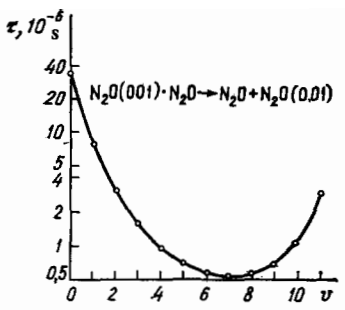


FIG. 13. Predissociation time of the $N_2O(001) \cdot N_2O$ van der Waals molecule vs the vibrational excitation of the weak bond.

this complex is determined by a dipole-dipole interaction associated with a partial transfer of a vibrational excitation to the unexcited molecule, so that after the rupture of the bond the originally unexcited molecule is in a vibrationally excited state, $N_2O(100)$. Figure 13 shows the predissociation time as a function of the vibrational excitation of the weak bond. Interestingly, this is not a monotonic dependence, and at high excitations of the weak bond the predissociation time of the molecule increases with increasing excitation. The reason for this effect is that at large excitations of the weak bond the distance between the molecules increases with increasing excitation. The dipole exchange interaction between the vibrational states of the molecule—the interaction responsible for the predissociation—therefore weakens with increasing excitation of the weak bond at high excitation levels of this bond, at which the anharmonicity of the vibrations for the weak bond is important. The net result is an increase in the decay time of the complex.

Comparison of the predissociation times in Fig. 13 with those shown in Fig. 14 for van der Waals molecules of another type and also with the data in Table XIII reveals that these times differ by several orders of magnitude. This difference is evidence that the predissociation time is very sensitive to the structure and properties of the van der Waals molecule. Yet another example of predissociation is that of

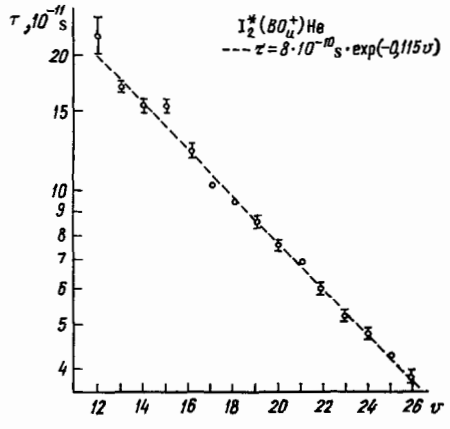


FIG. 14. Lifetime of the electronically excited $I_2^*$He van der Waals molecule with respect to predissociation as a function of the vibrational state of the iodine molecule.[114] The electronic state of this molecule is $BO_u^+$. The dashed line is an approximation of the predissociation time: $\tau = \tau_0 \exp(-0.115\,v)$, where $\tau_0 = 0.8$ ns.

the HD · Ar molecule for the first vibrational state of HD. The predissociation time of this state is approximately $10^{-11}$ s according to measurements[135] and calculations.[136]

Our analysis of the photodissociation of van der Waals molecules has so far been primarily concerned with clusters containing identical molecules. Extensive research has been carried out for molecules of the $AI_2$ type, where A is an inert gas atom or a hydrogen molecule.[120] This research has made it possible to determine the properties of the particular molecules. In contrast with the cases discussed above, electronic states are excited in these molecules. An important point is that the inert gas atom (or the hydrogen molecule) in van der Waals molecules of this type causes only a slight change in the interaction between the iodine atoms. The process can be described by

$$\left.\begin{aligned} I_2A\,(v=0)+\hbar\omega &\to I_2^*A\,(v'),\\ I_2^*A\,(v') &\to I_2^*\,(v_1')+A,\\ I_2^*\,(v_1') &\to I_2\,(v'')+\hbar\omega; \end{aligned}\right\} \qquad (8)$$

where A is the inert gas atom or the hydrogen molecule; $I_2$ corresponds to the ground state of the $XO_g^+$ ($B^3\Pi_u$) molecule; and $I_2^*$ corresponds to the electronically excited $BO_u^+$ ($B^3\Pi_u$) state. The vibrational excitation of the iodine molecule is shown in parentheses. As a result of predissociation, some of the vibrational excitation of the molecule is expended on its dissociation. The predissociation times in these cases are typically $10^{-11}$–$10^{-10}$ s. Figure 14 shows the predissociation time of the $I_2^*$He molecule as a function of the vibrational state of the iodine molecule.[112] The lifetime of this van der Waals molecule naturally increases with decreasing vibrational excitation of the iodine molecule.

Table XIV shows the predissociation times of these van der Waals molecules. With increasing atomic weight of the inert gas atom the lifetime of the complex decreases, since a more effective interaction between the inert gas atom and the iodine atom comes into play. In the interaction of the iodine molecule with the hydrogen molecule, additional pathways for energy exchange between the particles are opened up, with the result that the predissociation time decreases. Comparison with Table XIII shows that the interaction is less effective in these molecules, so that their predissociation times are more than two orders of magnitude longer than for the molecules in Table XIII.

Measurements of the fluorescence of the excited gas molecule formed as a result of this process ultimately yields

TABLE XIV. Predissociation times[112–115] of van der Waals molecules containing electronically and vibrationally excited iodine molecules, $I_2^*$ ($BO_u^+$ v).

| Molecule | v | τ, $10^{-11}$ s | Molecule | v | τ, $10^{-11}$ s |
|---|---|---|---|---|---|
| $I_2^*$He | 9 | 46 | $I_2^*$Ar | 15 | 3,7 |
| | 12 | 22 | $I_2^*H_2$ | 14 | 1,8 |
| | 14 | 15 | $I_2^*Ne_2$ | 12 | 10 |
| $I_2^*$Ne | 9 | 22 | $I_2^*$Ne·He | 9 | 21 |
| | 12 | 23 | | 12 | 10 |
| | 14 | 8.4 | | | |

TABLE XV. Properties of van der Waals molecules* having an iodine molecule as a component[116–118]

| Molecule | $I_2He$ | $I_2^*He$ | $I_2Ne$ | $I_2^*Ne$ |
|---|---|---|---|---|
| $\hbar\omega_e$, $cm^{-1}$ | 7,02±0,07 | 7,10±0,08 | 25,0±0,1 | 25,1±0,1 |
| $\hbar\omega_e x_e$, $cm^{-1}$ | 0,55±0,03 | 0,72±0,04 | 1,84±0,04 | 2,02±0,04 |
| $\alpha$, $Å^{-1}$ | 0,36±0,01 | 0,41±0,01 | 1,42±0,01 | 1,50±0,02 |
| $D_0$, $cm^{-1}$ | 18,8±0,6 | 14,2±0,6 | 73±1 | 66±1 |
| $D_e$, $cm^{-1}$ | 22,2±0,6 | 17,6±0,6 | 85,0±0,5 | 78±1 |

| Molecule | $I_2Ar$ | $I_2^*Ar$ | $I_2H_2$ | $I_2^*H_2$ | $I_2D_2$ | $I_2^*D_2$ |
|---|---|---|---|---|---|---|
| $\hbar\omega_e$, $cm^{-1}$ | 25,62±0,02 | 25,64±0,02 | 131 | 106 | 92 | 75 |
| $\hbar\omega_e x_e$, $cm^{-1}$ | 0,66±0,01 | 0,70±0,01 | 28 | 23 | 14 | 12 |
| $\alpha$, $Å^{-1}$ | 1,16±0,01 | 1,20±0,01 | — | — | — | — |
| $D_0$, $cm^{-1}$ | 237±3 | 223±3 | 92 | 74 | 108 | 87 |
| $D_e$, $cm^{-1}$ | 250±3 | 236±3 | 151 | 122 | 151 | 122 |

*Here $I_2$ corresponds to the $XO_g^+$ electronic ground state of the iodine molecule, and $I_2^*$ corresponds to the $BO_u^+$ excited state. The properties correspond to the weak bond.

the properties of a van der Waals molecule containing an iodine molecule in the ground and excited states.[116–118] Since the predissociation time of the complex is considerably shorter than its radiative lifetime ($10^{-6}$s), the fluorescence results from the decay of excited iodine molecles. The fluorescence therefore provides only indirect information about the properties of the cluster. The rupture energy of the weak bond can be determined reliably, for the following reason. The vibrational quantum number of the electronically excited iodine molecule is determined by the wavelength of the light which is absorbed, and the vibrational quantum number of the illuminated iodine molecule shows how much energy is expended on rupturing the weak bond during the predissociation. An important point is that the vibrational quantum number of the excited iodine molecule is several tens and can change, while the distribution of illuminated iodine molecules in vibrational states is related to the nature of the interaction in the excited van der Waals molecule during the predissociation. Furthermore, important information about the van der Waals molecule can be obtained from its absorption spectrum or, more precisely, from the shift of the absorption resonances for the free iodine molecule when it becomes bound in a cluster.

Table XV shows the results of an analysis of information of this type.[116–118] We see that the depth of the potential for the interaction of the iodine molecule with inert gas atoms is of the same order of magnitude as for the interaction of halogen atoms with inert gas atoms (Table III). The circumstance and the magnitude of the rupture energy of the weak bond show that the bond in these clusters is determined by the weak van der Waals interaction.

## 8. INTERACTIONS OF VAN DER WAALS MOLECULES

Van der Waals molecules in a gas can accelerate processes which occur in three-body collisions. Let us consider the three-body process

$$A + B + M \xrightarrow{\mathcal{K}} AB + M, \tag{9}$$

where the third particle, M, is required in order to carry off the excess energy. This process, which results in the formation of a bound state, can occur in a two-body collision with a van der Waals molecule

$$A + B \cdot M \xrightarrow{k} AB + M \tag{10}$$

In this case the collision with the van der Waals molecule actually involves the simultaneous collision with both components of the van der Waals molecule, since the weak bond in the van der Waals molecule does not alter the nature of the interaction of the particles during the collision.

Process (9) clearly occurs more efficiently than (10) if the rate constants for these processes satisfy the inequality

$$k\,[B \cdot M] \gg \mathcal{K}\,[B]\,[M]. \tag{11}$$

If thermodynamic equilibrium is maintained in the gas, this inequality can be written

$$\frac{k}{\mathcal{K}} \gg K_{eq}\ (T), \tag{12}$$

where the equilibrium constant is $K_{eq} = \{[B]\,[M]\}/[B \cdot M]$. The rate constants in (12) do not depend strongly on the temperature, while the equilibrium constant is an exponential function of the temperature: $K_{eq} \sim e^{-D/T}$ ($D$ is the dissociation energy of the van der Waals molecule). It follows that inequality (12) becomes progressively stronger as the gas temperature is lowered. Process (10) is thus more effective than (9) at low temperatures, $T \ll D$.

Essentially the only process of this type which has been studied is the attachment of an electron to a molecule. Armstrong and Nagra,[121] for example, studied the attachment of electrons to HCl and HBr molecules, finding results which could be explained only by assuming that the electrons became attached to $(HCl)_2$ and $(HBr)_2$ molecules at elevated pressures.

The only case of electron attachment to a van der Waals molecule which has been studied extensively both experimentally and theoretically is the formation of the negative oxygen molecule in various buffer gases. Let us analyze this process. In the absence of van der Waals molecules it occurs by the so-called Bloch-Bradbury mechanism through the

TABLE XVI. Rate constant for electron capture by van der Waals molecules.

| Molecule | $(^{18}O_2)_2$ | $(^{16}O_2)_2$ | $O_2 \cdot CO$ | $O_2 \cdot N_2$ | $O_2 \cdot CO_2$ | $O_2 \cdot C_2H_4$ | $O_2 \cdot C_2H_6$ | $O_2 \cdot C_3H_8$ | $O_2 \cdot n\text{-}C_4H_{10}$ | $O_2 \cdot neo\text{-}C_5H_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $K_{capt.}$, $10^{-9}cm^3/s$ | 5.0 | 4.0 | 2.8 | 1.3 | 8.0 | 5.0 | 8.0 | 2.0 | 2.0 | 20 |
| Reference*) | 124 | 124 | 124 | 124 | 125 | 125 | 126 | 126 | 126 | 125 |

*The rate constant for the overall process (10) is given in Ref. 124.

formation of an autoionization state:

$$\left.\begin{aligned} e + O_2 &\underset{1/\tau}{\overset{k^{(0)}_{capt}}{\rightleftarrows}} (O_2^-)^{**}, \\ (O_2^-)^{**} + M &\begin{cases} \xrightarrow{\xi k_{qu}} O_2^- + M, \\ \xrightarrow{(1-\xi)k_{qu}} O_2 + e + M, \end{cases} \end{aligned}\right\} \quad (13)$$

where $(O_2^-)^{**}$ is the autoionization state of the negative ion of the oxygen molecule, and M is a buffer-gas molecule. The rates of the corresponding processes (indicated above the arrows) are determined by analyzing the experimental results. The rate constant for the formation of the autoionization state, for example is[122] $k^{(o)}_{capt} = 3.0 \cdot 10\,cm^3/s$, and the decay time of the autoionization state is[122] $8.8 \cdot 10^{-11}$s [$k^{(0)}_{capt} = (4.8 \pm 0.6) \cdot 10^{-11}$ cm$^3$/sec, according to Ref. 123].

Van der Waals molecules in a gas create a new pathway for the attachment of an electron to an oxygen molecule:

$$\left.\begin{aligned} e + O_2 \cdot M &\underset{1/\tau_1}{\overset{k_{capt}}{\rightleftarrows}} (O_2^- \cdot M)^*, \\ (O_2^- \cdot M)^* &\xrightarrow{\frac{1}{\tau_2}} O_2^- + M, \\ (O_2^- \cdot M)^* + M &\xrightarrow{k_{qu}} O_2^- + M. \end{aligned}\right\} \quad (14)$$

At high buffer-gas densities this process occurs as a two-body process and is characterized by a rate constant $k_{capt}$. Table XV shows values of this rate constant. The probability for the detachment of an electron during the quenching of the $(O_2^- \cdot M)^*$ autoionization state is low, so we will ignore that process.

Under what conditions does process (14) primarily determine the rate at which electrons attach to oxygen molecules? The corresponding condition for a high buffer-gas density is

$$\frac{[O_2 \cdot M]}{[O_2]} > \frac{\xi k^{(0)}_{capt}}{k_{3\,capt}}. \quad (15)$$

Table XVII shows the buffer-gas densities $[M]_0$ at which the left and right sides of (15) are equal. The equilibrium constants for this process at room temperature were calculated by McMahon,[127] who analyzed the process in detail. Under the condition $[M] \gg [M]_0$ the attachment of the electron to the oxygen molecule occurs through the formation of a van der Waals molecule. This condition was derived under the assumption $k_{qu}\tau[M] \gg 1$, i.e., under the assumption that the autoionization state which is formed is quenched primarily as a result of collisions. Table XVI shows values of this parameter at the buffer-gas density $[M]_0$. This quantity is the ratio of the probability for the quenching of the autoionization state in a collision to the probability for the spontaneous decay of this state. We see that in most cases the mechanism of electron attachment due to van der Waals molecules is important precisely at the high pressures at which the attachment is a two-body process. For the n-$C_4H_{10}$ and neo-$C_5H_{12}$ molecules the contribution of the van der Waals mechanism at low pressures should be determined from (11). The quantity $k/(\mathcal{K}K_{eq})$—the ratio of the probability for electron attachment by mechanism (14) to the probability for attachment by mechanism (13) [see (9)–(11)]—is approximately unity in each case. In other words, the two channels are comparable in effectiveness.

Analysis of Table XVI shows that at pressures of the order of atmospheric the attachment of an electron to a molecule in a process involving van der Waals molecules contributes substantially to the rate of this process.

## 9. CONCLUSION

Van der Waals molecules are molecules with a weak bond in which the components retain their individuality. These entities have been recognized for a long time, but the scope of research on them has increased substantially over the past decade.

The sections of this review on photoionization, photodissociation, and the rotational spectra of van der Waals

TABLE XVII.

| M | $O_2$ | $CO_2$ | $C_2H_4$ | $C_2H_6$ | $C_3H_8$ | n-$C_4H_{10}$ | neo-$C_5H_{12}$ |
|---|---|---|---|---|---|---|---|
| $K_{eq}$, $10^{21}cm^{-3}$[127] | 2.5 | 5.0 | 5.0 | 2.9 | 2.1 | 4.5 | 2.4 |
| $[M]_0$, $10^{19}$ cm$^{-3}$ | 1.5 | 1.9 | 3.0 | 1.1 | 3.2 | 0.7 | 0.4 |
| $k_{qu} \cdot \tau [M]_0$ | 1.0 | 1.6 | 3.3 | 1.2 | 4.8 | 0.1 | 0.06 |

molecules, for example, contain information acquired during the past decade. The primary reason for this situation is the development of new experimental apparatus, which has made it possible to solve some fundamentally new problems.

Research on the various properties of van der Waals molecules, however, is presently uncoordinated. The studies of photoionization, photodissociation, and rotational spectra, for example, deal with different types of molecules for the most part, so that these studies do not complement each other, and they do not draw a common physical picture of the properties of van der Waals molecules. On the other hand, we are still in an early stage of this research, and the various directions presently being taken will presumably converge in the future to form a somewhat more unified research program.

The primary factor in the progress in research on van der Waals molecules in the future, as in the present, will be a continuing experimental sophistication, rather than applications. The development of new apparatus (tunable lasers, far-UV sources, quadrupole mass spectrometers, radiation and particle detectors, etc.) with better characteristics will make it possible to develop new experimental methods, which will furnish new information about the various entities and processes. There can be no doubt that the rapidly unfolding developments in the laboatory will present us in the very near future with fundamentally new information on various entities in atomic and molecular physics, including van der Waals molecules.


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